WET CHEMICAL ETCHING - BASICS

Before going into the specific issues such as the wet-chemical etching of certain substances, in the following chapters, this chapter would like to first explain the appropriate chemical basics of acids, bases and the principle etching mechanism for a better understanding.

Acids and Bases: Oxidation and Reduction

Autoprotolysis of Water

Pure water contains approx. $10^{-7}$ mol oxonium ($H_3O^+$) and hydroxide ($OH^-$) ions per litre at room temperature via the thermally activated endothermic autoprotolysis $2 H_2O \rightarrow H_3O^+ + OH^-$ which via

$$pH = -\log_{10}[H_3O^+]$$

corresponds to a pH-value of 7. The degree of auto-dissociation increases with the temperature, so the pH-value of 100°C of hot ultra-pure water is already about 6, corresponding to a ten-fold increased $H_3O^+$ concentration.

Acids

Acids as proton donors in aqueous solutions increase via the dissociation of protons (e.g. hydrochloric acid: $HCl + H_2O \rightarrow H_3O^+ + Cl^-$) the concentration of $H_3O^+$ ions, whereby the pH-value drops. A measure of the strength of an acid is defined as the degree of dissociation in aqueous solutions, defined via

$$pK_a = -\log_{10}\left(\frac{[dissociated \ acid]}{[undissociated \ acid]}\right)$$

by the $pK_a$ value. Very strong acids like $HClO_4$, $HI$, $HCl$ or $H_2SO_4$ are as an aqueous solution almost completely dissociated. The strong tendency of $H_3O^+$ ions to emit protons or to absorb electrons is responsible for the oxidising effect of acids.

Bases

Bases as proton acceptors increase the concentration of $OH^-$ ions in aqueous solutions. According to the law of mass action, the product $[H_3O^+][OH^-]$ remains constant at a given temperature, so that the $H_3O^+$ concentration decreases, consequently the pH rises. Analogous to acids, the strength of a base in aqueous solutions can be defined as

$$pK_b = -\log_{10}\left(\frac{[dissociated \ base]}{[undissociated \ base]}\right)$$

The tendency of $OH^-$ ions to emit an electron is due to the reducing effect of bases.

Conjugated Acid and Base Pairs

The release of protons by acids or the absorption of protons by bases is reversible, which results in a concentration and temperature-dependent equilibrium, as, for example, in the case of dilute acetic acid, expressed by the following equation:

$$CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_3O^+$$

water as a base of the proton absorbs acetic acid, while in the back reaction, the acetate ion as a base of the proton absorbs the oxonium ion, which acts as an acid. Thus in the acetic acid and water system, two conjugated acid-base pairs are in equilibrium.
### Numerical Values for PH, \( pK_s \) and \( pK_B \) Values of Selected Substances

<table>
<thead>
<tr>
<th>pH levels</th>
<th>( pK_s ) values of acids</th>
<th>( pK_B ) values of bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric acid (37%)</td>
<td>-1</td>
<td>-10</td>
</tr>
<tr>
<td>Gastric acid</td>
<td>2</td>
<td>-6</td>
</tr>
<tr>
<td>Hydrofluoric acid (50%)</td>
<td>2</td>
<td>-3</td>
</tr>
<tr>
<td>Cola (typ.)</td>
<td>2 - 3</td>
<td>-1.32</td>
</tr>
<tr>
<td>Fruit juices (typ.)</td>
<td>3 - 4</td>
<td>2.13</td>
</tr>
<tr>
<td>Tap water</td>
<td>7 - 8.5</td>
<td>3.14</td>
</tr>
<tr>
<td>Sodium hydroxide (1%)</td>
<td>13.5</td>
<td>3.75</td>
</tr>
<tr>
<td>Sodium hydroxide (30 %)</td>
<td>15</td>
<td>4.75</td>
</tr>
</tbody>
</table>

Table 6: Exemplary pH, \( pK_s \) and \( pK_B \) values of various substances. In the \( pK_s \) values column, the acid strength increases from bottom to top; in the \( pK_B \) values column analogue the base strength.

### Chemical Buffer

**Definition**

Chemical buffers are substances which, despite the addition or removal of H\_3O\(^+\) or OH\(^-\) ions, keep the pH-value of a solution largely constant at a certain value, thus ensuring, among other things, that the etching rate remains constant during wet-chemical etching. They fulfill this task by releasing both oxonium ions or hydroxide ions as their concentration decreases, as well as bonding or neutralizing them as their concentration increases.

In order to be able to fulfill both tasks, buffer solutions are weak, i.e. incompletely dissociated acids or bases, while their conjugated bases or acids are present in the solution.

**Examples**

In addition to the above-mentioned acetic/acetate buffers, the ammonium buffers (NH\_4\(^+\) + H\_2O \leftrightarrow NH\_3\(^+\) + OH\(^-\)) as well as the phosphate buffers are important for the maintenance of the intracellular pH value for the organism (H\_2PO\_4\(^-\) + H\_2O \leftrightarrow HPO\_4\(^2-\) + H\_3O\(^+\)) buffer systems.

### Complexing Agents

**Theory**

As the etching time progresses, the etched material continues to concentrate in the solution, especially in the immediate vicinity of the etched surface. The lower its solubility product in the etching medium, the more strongly the re-incorporation into the solid is promoted and the more the etching rate is therefore reduced or brought to a standstill.

The stable bonding of the etched atoms to a chemical complex which is sufficiently soluble in the etching mixture enables a constantly high etching rate. A complex is a structure in which a central atom (usually a metal ion =the etched element) having gaps in its electron configuration is surrounded by one or more molecules or ions (the ligands) each having at least one free electron pair available for bonding.

**Examples**

During the etching of gold in aqua Regia, the highly water-soluble chloroauroic acid (H\(\text{AuCl}_4\)) is produced, with cyanide solutions the Au(CN\_5\(^-\)) cyano complex. When platinum is etched in aqua Regia, chloroplatinic acid (H\(_2\text{PtCl}_6\)) is produced.
Partial Steps in Etching: Oxidation, Dissolution, Diffusion and Convection

**Oxidation**

The first reaction step in wet-chemical etching is the oxidation of the medium to be etched. This can be done either by complex formation or by oxidising components in the etching mixture, for which hydrogen peroxide or nitric acid are often used.

**Dissolution**

The oxidised material must quickly dissolve from the surface to be etched in order to allow rapid and homogeneous etching. Substances frequently used for etching of the oxides are hydrochloric acid, hydrofluoric acid, ammonium hydroxide or phosphoric acid.

**Diffusion**

At room temperature, atoms and molecules have average velocities of up to several 100 m/s. Due to the low average free length of path in liquids, the movement of atoms results in an undirected dithering which only very slowly smoothens concentration gradients.

**Convection**

Gas formation during etching, heat evolution by exothermic etching reactions, or mechanical agitation induces large-scale convection in the etching solution. Since diffusion alone is not sufficient, mainly this form of material transport contributes to a fast and spatio-temporal homogeneous etching.

Etching of Metals and Noble Metals

**Energy, Entropy and Enthalpy**

The acid etching of metals is essentially based on an oxidation of the metal via protons donated by the \( \text{H}_3\text{O}^+ \) hereby reduced to neutral hydrogen as follows:

\[
\text{metal} + \text{H}^+ \rightarrow \text{metal}^+ + \text{H}.
\]

If only energetic aspects of the etching were to be observed, only metals could be etched in which the above reaction takes place exothermically, the change in the internal energy \( \Delta U \) is thus negative. This condition satisfies by definition all metals with a normal potential \( E_0 \) smaller than that of the hydrogen, which is set to zero, that is to say all the base metals per definition.

However, the fact that noble metals with a positive normal potential such as the easily etchable copper can be etched despite an \( E_0 = +0.34 \) is because, as in all chemical reactions, the increase in entropy is important in addition to the reduction in energy in the question of whether a reaction is taking place. In physical terms, this is the case when the change in the free enthalpy \( \Delta F = \Delta U - T \Delta S \) is negative, that is, the product of temperature \( T \) and entropy change \( \Delta S \) is more positive than the change in the internal energy \( \Delta U \). A positive \( \Delta S \) is given, for example, by the increase in the number of translational and spatial degrees of freedom through the transition from the solid in the solution or the solutes into the gas phase.

**Electron Shells and Standard Potential**

Both the highly reactive alkali metals (Li, K, Na...), as well as many of the inert noble metals (Au, Ag, Pt,...) have an s-orbital with an unpaired electron. While alkali metals very easily release this electron (oxidation), noble metals have a comparably high ionisation energy (high positive standard potential).

The reason for this behaviour is as follows: Noble metals such as Au, Ag or Pt with a single electron in the s-orbital with the quantum number \( n \) (‘shell’) appear to have a completely occupied d-orbital with the quantum number \( n-1 \) (e.g. electron configuration of gold: [Xe]4f\(^{14}\)5d\(^{10}\)6s\(^{1}\)). This occupied d-orbital partially protrudes beyond the s-orbital and hereby spatially shields it against reactants. Additionally, from the point of view of the s-electron, the nuclear charge is only partially shielded from the extended d-orbital thus further increasing the bonding energy of the s-electron.

Some noble metals do not have an unpaired valence electron. Either the outer s-orbital is unoccupied (Palladium), or completely occupied with an electron pair (e.g. With iridium), both further increasing the first ionisation energy and the chemical stability. As a consequence, the only way to etch iridium is with hot (approx. 100°C) aqua Regia.
Fundamental Problems in Wet Etching

Under-etching and Resist Lift-off of Small Structures

A peeling of primarily small/narrow resist structures during wet chemical etching processes points towards under-etching of the resist with a decrease of the contact area between resist and substrate as a consequence.

Sometimes accompanied by elevated temperatures or/and gas formation, small resist structures lift off from the substrate during etching.

In case of isotropic etchants, the grade of under-etching cannot be minimised under a certain minimum: For any μm to be etched in depth, the etching will also proceed laterally under the resist. Only special etching mixtures for certain metals as well as spray etching allow a certain selectivity in the depth. If the extent of the under-etching is however much greater, this indicates a poor resist adhesion.

The resist adhesion can be improved with an optimised substrate pre-treatment, adapted soft bake parameters or/and a hardbake after the development. Such a hardbake above the softening point of the resist can lead to a better contact to the substrate. From 150°C, the thermal cross-linking of resin stabilises the resist structures, but increasingly complicates their subsequent removability.

Large-scale Resist Peeling

When Etching in Hydrofluoric Acid

During etching with HF or HF-containing mixtures, a large-scale resist lift-off is often seen after a certain etching duration or subsequent rinse. The reason for this is two parallel running mechanisms:

- The resist structures swell from a diffusing of hydrofluoric acid into the resist film.
- If the HF reaches the substrate and starts to attack it - as is the case with, for example, SiO\textsubscript{2} or glass - the resist film lifts off (Fig. 117).

Thus, no proper resist adhesion problem exists at least to explain this effect. Instead, the barrier for F- ions which diffuse in the direction of the substrate and thus the resist film thickness must be increased, where a good approximation is: A factor of two in the film thickness quadruples the possible etching time.

In addition, the use of buffered (BHF) instead of unbuffered HF is helpful because, in the case of BHF, the active ions responsible for etching are HF\textsubscript{2}- ions which are less mobile (slower diffusion) in the resist film.

Special Cases

In the case of substrates metallised on both sides in which both metals have a different standard potential (e.g. silver on one side and aluminium on the other), a galvanic element forms in aqueous solutions. On the one hand, hydrogen gas can form on the surface of the metal/resist which can lift off the overlying resist film. In this case, a closed protective resist film helps (any photoresist, or the photoinitiator-free cost effective AZ® 520D) on the opposite side of the substrate.
Organic Solvents

Almost all organic solvents dissolve positive and image reversal resists in a short time. Only cross-linking negative resists, such as the AZ® nLOF 2000 series or thermally cross-linked positive or reversal resists, are stable against organic solvents within limits. Dissolution of the resist structures then no longer takes place, however, the resist mask may peel from the substrate.

Acids

Hydrochloric acid is a comparable non-critical medium for photoresist masks. When etching with hydrofluoric acid, their permeability in photoresist layers is taken into account. Un-buffered or buffered hydrofluoric acid can easily be used with sufficiently thick photoresist films or short etching times for many etching processes. Strongly oxidising acids such as HNO₃-containing mixtures or etching mixtures of H₂SO₄ and H₂O strongly attack photo-resist. A thermal cross-linking of positive resists or the use of negative cross-linking negative resists can significantly increase the stability of the resist mask.

Bases

Photoresists are considerably less stable in alkaline media than in acidic solutions. Even 1 to 2% sodium or potassium hydroxide solution attack positive resist structures. With higher concentrations, cross-linked negative resists also tend to lift off from the substrate.

With a masking using conventional positive or negative resists, for example, neither anisotropic silicon etching nor alkaline etching of thicker aluminium films is possible.
### Our Photoresists: Application Areas and Compatibilities

<table>
<thead>
<tr>
<th>Recommended Applications</th>
<th>Resist Family</th>
<th>Photosists</th>
<th>Resist Film Thickness</th>
<th>Recommended Developers</th>
<th>Recommended Removers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Improved adhesion for wet etching, no focus on steep resist sidewalls</td>
<td>AZ® 1500</td>
<td>AZ® 1505</td>
<td>0.5 µm</td>
<td>AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>AZ® 1512 HS</td>
<td>1.0 - 1.5 µm</td>
<td></td>
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<td></td>
<td></td>
<td>AZ® 1514 H</td>
<td>1.2 - 2.0 µm</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>AZ® 1518</td>
<td>1.5 - 2.5 µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spray coating</td>
<td>AZ® 4500</td>
<td>AZ® 4533</td>
<td>3 - 5 µm</td>
<td>AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>AZ® 4562</td>
<td>5 - 10 µm</td>
<td></td>
<td></td>
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<tr>
<td>Steep resist sidewalls, high resolution and aspect ratio for e.g. dry etching or plating</td>
<td>AZ® P4000</td>
<td>AZ® P4110</td>
<td>1 - 2 µm</td>
<td>AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>AZ® P4330</td>
<td>3 - 5 µm</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>AZ® P4620</td>
<td>6 - 20 µm</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>AZ® P4903</td>
<td>10 - 30 µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elevated thermal softening point and high resolution for e.g. dry etching</td>
<td>AZ® 4990</td>
<td>AZ® PL 177</td>
<td>3 - 8 µm</td>
<td>AZ® 351B, AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>AZ® PL 177</td>
<td>1 - 15 µm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Our Developers: Application Areas and Compatibilities

#### Inorganic Developers

**AZ® Developer** is based on sodium phosphate and –metasilicate, is optimized for minimal aluminum attack and is typically used diluted 1 : 1 in DI water for high contrast or undiluted for high development rates. The dark erosion of this developer is slightly higher compared to other developers. **AZ® 351B** is based on buffered NaOH and typically used diluted 1 : 4 with water, for thick resists up to 1 : 3 if a lower contrast can be tolerated. **AZ® 400K** is based on buffered KOH and typically used diluted 1 : 4 with water, for thick resists up to 1 : 3 if a lower contrast can be tolerated. **AZ® 303** specifically for the AZ® 111 XFS photoresist based on KOH / NaOH is typically diluted 1 : 3 - 1 : 7 with water, depending on whether a high development rate, or a high contrast is required.

#### Metal Ion Free Developers

**AZ® 326 MIF** is 2.38 % TMAH- (Tetramethylammoniumhydroxide) in water.
AZ® 726 MIF is 2.38 % TMAH- (Tetramethylammoniumhydroxide) in water, with additional surfactants for rapid and uniform wetting of the substrate (e. g. for puddle development)

AZ® 826 MIF is 2.38 % TMAH- (Tetramethylammoniumhydroxide) in water, with additional surfactants for rapid and uniform wetting of the substrate (e. g. for puddle development) and other additives for the removal of poorly soluble resist components (residues with specific resist families), however at the expense of a slightly higher dark erosion.

Our Removers: Application Areas and Compatibilities

AZ® 100 Remover is an amine solvent mixture and standard remover for AZ® and Ti photoresists. To improve its performance, AZ® 100 remover can be heated to 60 - 80°C. Because the AZ® 100 Remover reacts highly alkaline with water, it is suitable for this with respect to sensitive substrate materials such as Cu, Al or ITO only if contamination with water can be ruled out.

TechniStrip® P1316 is a remover with very strong stripping power for Novolak-based positive resists, epoxy-based coatings, polyimides and dry films. At typical application temperatures around 75°C, TechniStrip® P1316 may dissolve cross-linked resists without residue also, e.g. through dry etching or ion implantation. TechniStrip® P1316 can also be used in spraying processes. For alkaline sensitive materials, TechniStrip® P1331 would be an alternative to the P1316. Nicht kompatibel mit Au oder GaAs.

TechniStrip® P1331 can be an alternative for TechniStrip® P1316 in case of alkaline sensitive materials. TechniStrip® P1313 is not compatible with Au or GaAs.

TechniStrip® N555 is a stripper with very strong dissolving power for Novolak-based negative resists such as the AZ® 15 nXT and AZ® nLOF 2000 series and very thick positive resists such as the AZ® 40 XT. TechniStrip® N555 was developed not only to peel cross-linked resists, but also to dissolve them without residues. This prevents contamination of the basin and filter by resist particles and skins, as can occur with standard strippers. TechniStrip® N555 is not compatible with GaAs.

TechniClean™ CA25 is a semi-aqueous proprietary blend formulated to address post etch residue (PER) removal for all interconnect and technology nodes. Extremely efficient at quickly and selectively removing organo-metal oxides from Al, Cu, Ti, TiN, W and Ni.

TechniStrip™ NFS2 is a very effective remover for negative resists (liquid resists as well as dry films). The intrinsic nature of the additives and solvent make the blend totally compatible with metals used throughout the BEOL interconnects to WLP bumping applications.

TechniStrip™ Micro D2 is a versatile stripper dedicated to address resin lift-off and dissolution on negative and positive tone resist. The organic mixture blend has the particularity to offer high metal and material compatibility allowing to be used on all stacks and particularly on fragile III/V substrates for instance.

TechniStrip™ MLO 07 is a highly efficient positive and negative tone photoresist remover used for IR, III/V, MEMS, Photonic, TSV mask, solder bumping and hard disk stripping applications. Developed to address high dissolution performance and high material compatibility on Cu, Al, Sn/Ag, Alumina and common organic substrates.

Our Wafers and their Specifications

Silicon-, Quartz-, Fused Silica and Glass Wafers

Silicon wafers are either produced via the Czochralski- (CZ-) or Float zone- (FZ-) method. The more expensive FZ wafers are primarily reasonable if very high-ohmic wafers (> 100 Ohm cm) are required.

Quartz wafers are made of monocrystalline SiO₂, main criterion is the crystal orientation (e. g. X-, Y-, Z-, AT- or ST-cut)

Fused silica wafers consist of amorphous SiO₂. The so-called JGS2 wafers have a high transmission in the range of ≈ 280 - 2000 nm wavelength, the more expensive JGS1 wafers at ≈ 220 - 1100 nm.

Our glass wafers, if not otherwise specified, are made of borosilicate glass.

Specifications

Common parameters for all wafers are diameter, thickness and surface (1- or 2-side polished). Fused silica wafers are made either of JGS1 or JGS2 material, for quartz wafers the crystal orientation needs to be defined. For silicon wafers, beside the crystal orientation (<100> or <111>) the doping (n- or p-type) as well as the resistivity (Ohm cm) are selection criteria.

Prime-, Test-, and Dummy Wafers

Silicon wafers usually come as „Prime-grade“ or „Test-grade“, latter mainly have a slightly broader particle specification. „Dummy-Wafers“ neither fulfill Prime- nor Test-grade for different possible reasons (e. g. very broad or missing specification of one or several parameters, reclaim wafers, no particle specification) but might be a cheap alternative for e. g. resist coating tests or equipment start-up.

Our Silicon-, Quartz-, Fused Silica and Glass Wafers

Our frequently updated wafer stock list can be found here: www.microchemicals.com/products/wafers/waferlist.html

Further Products from our Portfolio

Plating

Plating solutions for e. g. gold, copper, nickel, tin or palladium: www.microchemicals.com/products/electroplating.html

Solvents (MOS, VLSI, ULSI)

Acetone, isopropyl alcohol, MEK, DMSO, cyclopentanone, butylacetate, ... www.microchemicals.com/products/solvents.html

Acids and Bases (MOS, VLSI, ULSI)

Hydrochloric acid, sulphuric acid, nitric acid, KOH, TMAH, ... www.microchemicals.com/products/etchants.html

Etching Mixtures

for e. g. chromium, gold, silicon, copper, titanium, ... www.microchemicals.com/products/etching_mixtures.html
Further Information


Our Photolithography Book and -Posters

We see it as our main task to make you understand all aspects of microstructuring in an application-oriented way. At present, we have implemented this claim with our book Photolithography on over 200 pages, as well as attractively designed DIN A0 posters for your office or laboratory. We will gladly send both of these to you free of charge as our customer (if applicable, we charge shipping costs for non-European deliveries):

www.microchemicals.com/downloads/brochures.html
www.microchemicals.com/downloads/posters.html

Thank you for your interest!

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